MEMO

Date:

To: A. M. Smith

From: H. S. Tung => Clammer

Subject: Monthly Status Report - G32,

Technical Objectives:

Genetron 32 - To develop vapor phase process for the manufacture of HFC-32.

Topics in this report:

1. Catalyst screening:

(a) Cr_2O_3/Al_2O_3(40/60 wt%) co-extrudate

(b) Cr_2O_3/Al_2O_3(78/22 wt%) co-extrudate

Accomplishments:

1. Vapor phase HFC-32 process:

Methylene chloride is used as feed to make difluoromethane (HFC-32). Two catalysts have been screened to study this reaction. The results are presented as follows:

(a) Cr_2O_3/Al_2O_3(40/60 wt%) co-extrudate:

This catalyst, which was originally developed for making HCFC-123 and 124, was studied for fluorination of methylene chloride. The reaction appeared to be very clean. The major by-product was chlorofluoromethane (HCFC-31). The underfluorinated HCFC-31 can be recycled to make more HFC-32. The other by-product was tentatively identified as chloromethane(HCC-40). HCC-40 was found in GC-MS analysis. It is not known how the HCC-40 was formed to date. It could be present in the feed. The detailed analysis of impurities in the methylene chloride is currently undertaken.

The results of two different temperatures are listed in Table 1. The reactions were conducted at 275 and 300 °C at 50 psig. The HF/CH_2Cl_2 mole ratio was 4, lower mole ratio produced more underfluorinated HCFC-31. At 275 °C, the conversion was 82% with 89.3% HFC-32 selectivity. The productivity of this catalyst was about 10 lbs HFC-32/hr/ft^3. At 300 °C, shorter contact time (10 seconds) was used. As a result, conversion and selectivity for 32 were somewhat lower, 77% and 84.7% respectively, but the productivity was higher, 13.6 lbs/hr/ft^3.

(b) Cr_2O_3/Al_2O_3 (78/22 wt%) co-extrudate:

This catalyst contains more chrome than the above catalyst and was originally developed for the HFC-134a and HFC-125 processes. It is anticipated to be more active than the above (40/60 Cr/Al) catalyst.

The reaction was conducted under conditions similar to those indicated in the above section. The results are listed in Table 2. The reaction was again very clean. At 275 °C and 11 seconds contact time, it gave 82% conversion with 90.9% HFC-32 selectivity. The productivity was 15.5 lbs HFC-32/hr/ft^3 catalyst.

Both catalysts studied above showed slight deactivation after on-stream for more than 3 days. More detailed study is required to determine the catalyst stability.

Conclusions:

1. Vapor phase HFC-32 process using methylene chloride as starting material appeared to be feasible. The co-extruded Cr_2O_3 and Al_2O_3 catalysts appeared to be active and selective catalysts. The ~~major by-product was the underfluorinated HCFC-31.~~ The productivity was greater than 10 lbs HFC-32/hr/ft^3 catalyst without recycle of 31.

Future Plans:

1. Determine short term (250-500 hrs) catalyst stability for the Cr_2O_3/Al_2O_3 (78/22 wt%) catalyst.

2. Determine catalyst performance at high pressure.

3. Screen other catalysts such as Calsicat's Cr_2O_3 and Ni-Cr/AlF_3 catalysts.

4. Variables study and long term catalyst life study for the best catalyst if required.

Table 1

Fluorination of Methylene Chloride

Catalyst:	Cr_2O_3/Al_2O_3(40/60 wt%) co-extrudate	
Pressure:	50 psig	
HF/CH_2Cl_2 mol ratio:	4	
Temperature(°C):	275	300
Contact Time(sec):	16	10
Conversion % G30:	82	77
Selectivity(%):		
32	89.3	84.7
31	10.6	15.2
40(?)	0.1	0.1
Productivity(lbs/hr/ft^3):		
32	10.3	13.6

Table 2

Fluorination of Methylene Chloride

Catalyst:	Cr_2O_3/Al_2O_3 (78/22 wt%) co-extrudate	
Pressure:	50 psig	
HF/CH_2Cl_2 mol ratio:		4
Temperature (°C):		275
Contact Time (sec):		11
Conversion % G30:		82
Selectivity (%):		
	32	90.9
	31	9.1
	40 (?)	0.05
Productivity ($lbs/hr/ft^3$):		
	32	15.5

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GENETRON PROCESS DEVELOPMENT

MONTHLY STATUS REPORT

SAMPLE PREPARATION

HFC-32/125/143A

A. M. SMITH

-- ALLIED-SIGNAL INC --

-- CONFIDENTIAL --

AlliedSignal CONFIDENTIAL

MEMO

Date:

To: A. M. Smith

From: H. S. Tung

Subject: Monthly Status Report - G32,

Technical Objectives:

Genetron 32 - To develop vapor phase process for the manufacture of HFC-32.

Topics in this report:

1. Results of high pressure studies.

Accomplishments:

1. High pressure studies:

(a) Catalyst: Cr_2O_3/Al_2O_3(78/22 wt%) co-extrudate.

As indicated in my and reports, fluorination of methylene chloride to make HFC-32 has been demonstrated using the above-identified catalyst. The previous studies were conducted at 50 psig. Since HCl has to be removed from the product stream after the reactor, reflux of HCl is required in the distillation column. Reflux of HCl at low pressure(50 psig) requires very low temperature, translating into expensive refrigeration system. High pressure reaction followed by high pressure distillation are necessary for an economical process.

This study was to determine the feasibility of the vapor phase HFC-32 process at high pressures. Two high pressures, 200 and 225 psig, were chosen for study. The same reactor and catalyst as those used previously at 50 psig were used. The temperature was 275 °C. The feed rates were 60g/h methylene chloride and 58.2 g/h HF, the same as those at 50 psig. For given feed rates, increasing pressure increases contact time. Higher feed rate, 90 g/h CH_2Cl_2 and 87.3 g/h HF, were also studied at 225 psig.

The results are listed in Table 1. For the fixed feed rates, pressure changes from 50 to 200 and 225 psig changed contact time from 11 seconds to 36 and 40 seconds respectively. Pressure changes did not seem to change the conversions, selectivities and productivities. Increasing feed rates by 50% at 225 psig reduced conversion from 69.6% to 61.3%, but increased productivity from 11.8 to 14.9 lbs 32/hr/ft³. Faster feed rates at high pressure seemed to be beneficial.

Conclusions:

1. High pressure vapor phase HFC-32 process has been demonstrated. It appeared to be a good process.
2. Pressure changes did not affect the conversion, selectivities or the catalyst productivity.
3. High pressure and shorter contact time gave higher catalyst productivity.

Future Plans:

No future plan is scheduled for this reaction in the 1/2" reactor. HFC-32 sample preparation will be started in P. Clemmer's 4" reactor next month.

Table 1

Fluorination of Methylene Chloride

CH_2Cl_2 + HF ------> CH_2F_2

Catalyst: Cr_2O_3/Al_2O_3 (78/22 wt%) co-extrudate; 110 ml; 1/2" reactor d.

Pressure (psig):	50	200	225	225
HF/CH_2Cl_2 mol ratio:	4	4	4	4
Temperature (°C):	275	275	275	275
Contact Time (sec):	11	36	40	26
Conversion % G30:	71.3	70.4	69.6	61.3
Selectivity (%):				
32	81.9	80.9	80.9	77.3
31	18	19	18.9	22.6
40 (?)	0.05	0.05	0.05	0.05
Productivity ($lbs/hr/ft^3$):				
32	12.2	11.9	11.8	14.9
31	3.5	3.7	3.6	5.7

Feed rates: For 11, 36 and 40 seconds c.t. at 50, 200 and 225 psig, respectively, the feed rates were 60 g/h CH_2Cl_2 and 58.2 g/h HF.
For 26 seconds c.t. at 225 psig, the feed rates were 90 g/h CH_2Cl_2 and 87.3 g/h HF.

Allied Signal

Memorandum

Buffalo Research Laboratory
Buffalo, New York

ALLIED-SIGNAL, INC. - CONFIDENTIAL

DATE:

TO: H.S. Tung/A.M. Smith

FROM: P.G. Clemmer

SUBJECT: HFC-125/32 Sample Preparation and Process Development:

ACCOMPLISHMENTS:

1. Redistilled crude HFC-125 to produce 600 lbs total of 99.5%+ purity HFC-125.
2. Finished design work required to convert to HFC-32 production

Conversion to HFC-32 Production

Only 200 lbs. has been delivered out of 2000 lbs. of HFC-32 ordered from Halocarbon. Because we currently have enough HFC-125 for samples for the 1st Quarter, we will begin HFC-32 production next month and continue until at least the end of March. By the end of March we anticipate producing a minimum of 300 lbs. of product-quality HFC-32.

The necessary equipment modifications have been designed, with modifications expected to be complete by   The major modification in equipment consists of installation of a recycle line for continuous recycle of still bottoms. The purpose of this recycle is to demonstrate the feasibility of running this process with recycle, and to increase production of HFC-32. At the same time, the recycle stream will eliminate storage of the $HF/CH_2Cl_2/CH_2ClF$ from the still bottoms.

Figure 1 shows the flow diagram and stream summary. Flowrates and reaction conditions are based on H.S. Tung data with the following assumptions: 1) Methylene chloride conversion will be 70% per pass, 2) ratio of HFC-32 to HCFC-31 in the rxr outlet will be 4:1, 3) HFC-32 productivity will be about 11 $\#/hr/ft^3$, and 4) the capacity of the distillation column cooling will limit HFC-32 production to about 2 lbs/hr.

The reactor and catalyst to be used are the same as used for making HFC-125:

Reactor inner diameter:	4.026 in.
Reactor total inner length:	36 in.
Catalyst bed length:	24 in.
Catalyst volume:	5000 cc
Catalyst in reactor:	78/22 wt ratio Cr_2O_3/Al_2O_3

The reactor is situated in a fluidised sandbath for temperature control.

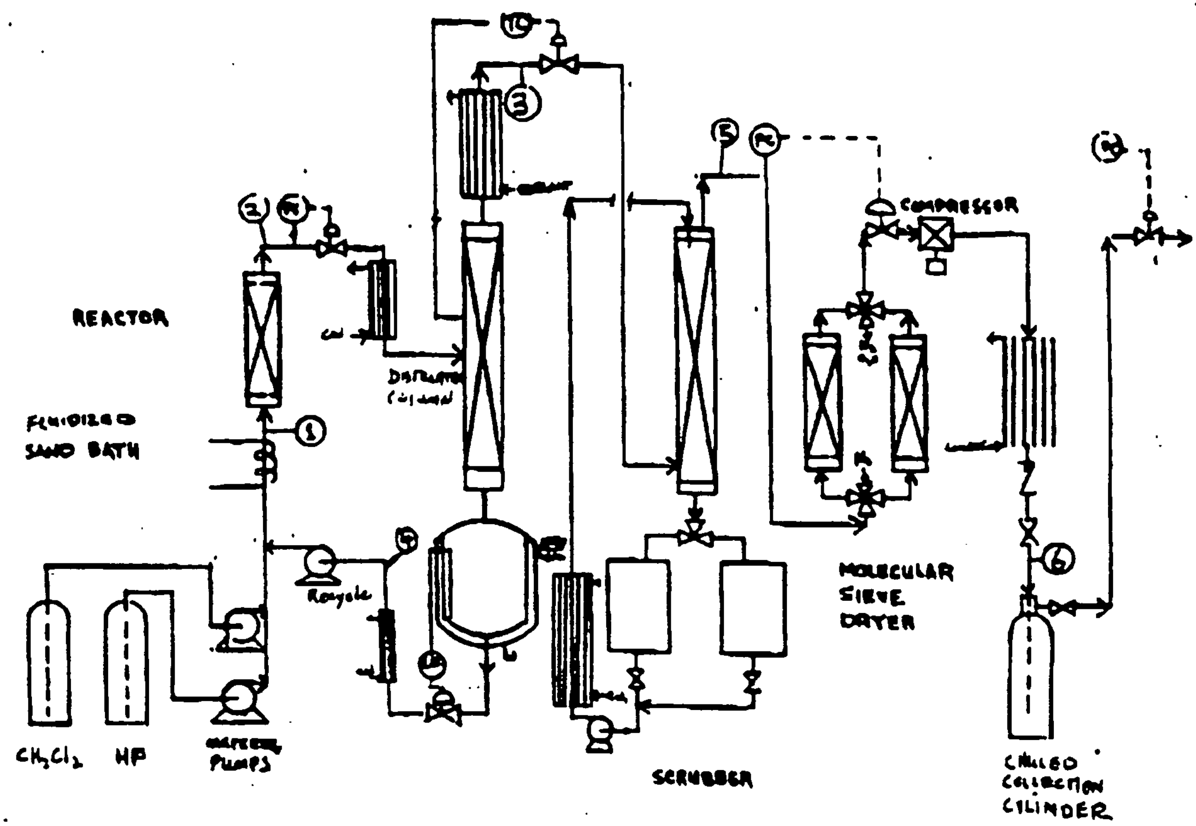
Inventory of Products

Future Plans: **Target Date:**

1.
1.

2. Complete equipment modifications for HFC-32 production
3. Test performance of 78 wt% Cr_2O_3/22 wt% Al_2O_3 in
   5 L reactor for HFC-32 production with recycle
4. Produce 300 lbs. of crude HFC-32

Paul Cl[illegible]



STREAM SUMMARY

Note: All temperatures and pressures are approximate; flowrates may vary.
Flowrates given in lbs/hr and (lbmole/hr).

Component	MW	(1) Rxr Inlet	(2) Rxr Outlet	(3) Distillate	(4) Recycle	(5) Scrub. out	(6) Product
HF	20	5.0 (0.25)	3.5 (0.18)	0	3.5 (0.18)	0	0
CH_2Cl_2	85	4.7 (0.055)	1.4 (0.017)	0	1.4 (0.017)	0	0
CH_2ClF	68.5	0.5 (0.0073)	0.5 (0.0073)	0	0.5 (0.0073)	0	0
CH_2F_2	52	0	2.0 (0.039)	2.0 (0.039)	0	2.0 (0.039)	2.0 (0.039)
HCl	36.5	0	2.8 (0.077)	2.8 (0.077)	0	0	0
Water	18	0	0	0	0	0.02 (0.001)	0
Stream Conditions							
Temp.	°C	275	275	-10	20	20	-20
Pressure	PSIG	200	200	130	130	5	45

<u>Scrubber caustic usage and waste discharge</u>
Average feedrate of 45% KOH: 9.4 lbs/hr
The 45% KOH is mixed with water to give a 10% KOH solution in the scrubber.
Approximate discharge rate of neutralized scrubber solution: 37 lbs/hr
(27 gallons discharged approximately once/7 hrs)

Composition (wt%) of neutralized scrubber solution:
91% water
9% KCl
<0.1% KOH
<100 ppm (est.) total organic (Mostly CH2F2; possible trace amounts of CH2ClF and CH2Cl2)

FIGURE 1: FLOW DIAGRAM AND STREAM SUMMARY FOR LABORATORY HFC-32 PRODUCTION

TABLE 1: CURRENT INVENTORY FOR THE BENCHSCALE PILOT PLANT

<u>Other inventory</u>

HFC-32	99.98%	50 lbs

TABLE 2: RECORD OF SAMPLES PROVIDED

Samples Provided

Date	Composition	Cyl.# or Source	Amount	Person
	HFC-32	Halocarbon	100 lbs.	"
	HFC-32	Halocarbon	50 lbs.	"

TOTAL HFC-32 SAMPLES: 150 lbs.